

## SYNTHETIC ZINC SULFIDE POLYTYPE CRYSTALS\*

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### ABSTRACT

Polytype crystals of ZnS or SiC consist of structures based on unit cells whose  $[c]$  axis spacing is some multiple of the number of layers on one atom sort contained in the simple hexagonal (2-layer) or rhombohedral (3-layer) polymorph prototypes. Known examples of polytypism in ZnS and SiC are summarized, and their genesis as a result of introducing periodic breaks in the stacking sequence of hexagonal layers is emphasized, as distinct from occasional or random (non-periodic) breaks which produce diffuse scattering of  $x$ -rays. Vapor phase grown ZnS crystals have complex growth habits and are shown to consist of mixed structures in the majority of cases regardless of external morphology, so that coalescence of different structures in our synthetic crystals is on a much finer scale than observed for the natural ZnS polytypes or for SiC. In addition to intimate mixtures of 2- and 3-layer structures—wurtzite and zincblende (or rhombohedral, Buck and Strock)—the vapor phase grown crystals also show the Frondel and Palache 4- and 6-layer polytype structures as minor phases in the same crystal. In one small crystal ( $0.01 \times 0.1$  mm), 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 11-layered structures have been observed. Many crystals show very intense diffuse  $x$ -ray reflections for planes in zones for which  $(h+2k)$  is not divisible by 3, which is not observed in the natural polytypes, but in natural wurtzite crystals from Thrace by Jagodzinski and Laves. The development of a  $TB$  system of notation is introduced as a means of relating periodic sequence breaks to polytype structures. This is based on the orientation of  $ZnS_4$  tetrahedra in adjacent layers of the structure—and is generally applicable to similar structures. The value  $N^*$  defines the layer where a break occurs and for each value of  $N^*$  a specific structure is derived. It is being related to impurity content of crystal growing atmospheres and growth habits.

### POLYTIPIISM IN ZINC SULFIDE

The three new crystal modifications of zinc sulfide, recently reported by C. Frondel and C. Palache (1) are the structural equivalents of three well known silicon carbide structures. In the nomenclature of L. Ramsdell (2) they are  $4H$  and  $6H$  (i.e. four and six layer hexagonal lattice unit cells) and  $15R$  (i.e. a five layer rhombohedral lattice unit cell, but referable for comparison with the others to a 15-layer hexagonal cell). Crystals in which these structures have been identified were discovered in clay-ironstone concretions near Etna, Allegheny County, Pennsylvania, by D. M. Seaman and H. Hamilton (3).

Frondel and Palache have described their new ZnS structures as *polymorphs*, and Ramsdell continually refers to the SiC modifications interchangeably as *types* or *polymorphs*. In the present paper we adhere to the suggestion of N. W. Thibault (4) and follow Baumhauer (5) in referring to the various modifications of ZnS and SiC as polytypes or as

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examples of "polytypism." Frondel and Palache have stated that ordinary wurtzite is the prototype of the "polymorphs" described by them. Their statement is true for the  $4H$  and  $6H$  structure but is not true for  $15R$ , since the latter is based on a rhombohedral lattice. The prototype of  $15R$  would be, at the time of their paper, a hypothetical rhombohedral modification of ZnS. Since a simple  $3R$  polymorph of ZnS has now been discovered and reported by D. Buck and L. W. Strock (6), we have a more complete understanding of their structural relationship and can use a more restricted nomenclature in describing them. Specifically, we restrict the term *polymorph* to structures characterized by different lattices; for example, in ZnS these are cubic face centered *sphalerite*, hexagonal close packed *wurtzite* and rhombohedral (*new modification found in vapor phase grown crystals*). The term *polytype* is any possible structural modification which alters the  $[c]$  axis dimension of the smallest unit cells referable to the above lattice types by some multiple of a single layer, in the case of ZnS and SiC, without altering the structure in the plane perpendicular thereto. This is simply a more precise restatement of Baumhauer's definition of "polytypism"\* in light of more recent knowledge regarding these structures. Structures based on the smallest unit cells of the polymorphs are thus prototypes of the polytypes. Consideration of any more general aspect and examples of polytypism will be discussed elsewhere. Doubling or trebling the  $[c]$  axis spacing produces 4-layer and 6-layer polytypes respectively from the *prototype wurtzite* in case of ZnS, and from a *hypothetical*†  $2-H$  *prototype* in case of SiC. The prototype of a 15-layer polytype is the new rhombohedral polymorph in the case of ZnS. We have not seen any reference to the corresponding polymorph of SiC.

Our work on ZnS crystals grown from the vapor phase has shown that the phenomenon of polytypism, in case of natural ZnS, is only one limited phase of the much broader problem of its crystal growth and that there is not complete parallelism between the structural phenomena exhibited by ZnS and SiC.

#### POLYTYPISM IN SILICON CARBIDE

Many more polytypes have been discovered for SiC than for ZnS,

\* "Polytypism" is defined by Baumhauer (p. 253) as a special example of polymorphism whereby different crystallographic and molecular structures of a substance, and thus essentially different modifications, are involved; for which, however, the axial ratio remains unchanged so that only a difference in crystal habit seems to exist. It should be noted that Baumhauer's original definition is based on a critical study of the crystal faces observed on 3 types of SiC, and their internal symmetry as determined by  $x$ -ray Laue photographs and not on structural studies or even cell size measurements.

† No  $2-H$  or wurtzite type SiC structure has been reported.

e.g. 14 are listed by L. S. Ramsdell and J. A. Kohn (7). The 14 modifications are: cubic; four hexagonal polytypes  $4H$ ,  $6H$ ,  $8H$ ,  $10H$ ; and nine rhombohedral polytypes  $15R$ ,  $21R$ ,  $27R$ ,  $33R$ ,  $51R_a$ ,  $51R_b$ ,  $75R$ ,  $84R$  and  $87R$ . L. S. Ramsdell and R. S. Mitchell (8) have since reported a  $19H$  structure, and announced the existence of 141, 168, 192 layer structures based on a rhombohedral lattice as determined on Buerger precession films. Further, G. S. Zhdanov and Z. V. Minervina (9) have reported a rhombohedral modification with 270-layers, and G. Honjo, S. Miyake and T. Tomito (10) a 594-layer rhombohedral structure. There is, thus, experimental evidence for the existence of at least 20 different SiC structures at present. These include the modifications described by Baumhauer as Types I, II, and III, which are the above listed  $15R$ ,  $4H$ , and  $6H$ , respectively.

#### POLYTYPISM AS EXAMPLE OF PERIODIC BREAKS IN HEXAGONAL STACKING SEQUENCE

The various polytypes may be derived from their prototype polymorphs by the introduction of breaks in the normal stacking sequence of the prototypes at periodic intervals along  $[c]$ . For example, breaking the hexagonal wurtzite sequence  $ABABAB$  to  $ABACABAC \dots$  generates the  $4H$  polytype sequence  $ABAC$ . Similarly, breaking the sequence  $ABCABC A \dots$  (which is cubic) to  $ABCACBA \dots$  generates the  $6H$  hexagonal polytype sequence  $ABCACB$ . These relationships are conveniently and clearly visualized, as done by L. S. Ramsdell (2), by plotting the positions of either atom sort of the structure on the plane (1120), and drawing lines between nearest neighbors in adjacent horizontal layers intersecting this plane. The lines drawn (with exception of cubic or  $3R$ ) are zigzag or Ramsdell diagrams. The five layer rhombohedral ZnS polytype thus consists of breaks at the third and fifth layers, in the otherwise linear sequence of cubic or simple rhombohedral structures. The 16th layer begins a fourth 32-sequence cycle at the same geometrical type of position, so that a 15-layer hexagonal cell may also be used to describe this structure. It is designated as  $15R$  to state both the number of layers in the equivalent hexagonal cell, and that its lattice is rhombohedral.

We may look upon these sequence breaks as disorders in the fundamentally simple sequence of stacking up hexagonal net layers. In the case of the natural ZnS polytypes such disorders are highly periodic, i.e. an *ordered disordered*. This is also true of SiC structures.

#### RANDOM BREAKS IN STACKING SEQUENCE IN ZNS

H. Jagodzinski and F. Laves (11) called attention to an apparent dif-

ferent sort of disorder in natural wurtzite from Thrace, which causes elongation of  $x$ -ray diffraction single crystal reflections from certain planes. Other spots in their spectra were identified as produced by twins oriented with respect to the main specimen. The cause of the diffuse  $x$ -ray reflections was attributed to disorder in the  $[c]$  direction of the wurtzite crystals, and designated as "one dimensional disorder." Jagodzinski and Laves recognized their observation on natural wurtzite to be an example of the same phenomenon encountered by O. S. Edwards and H. Lipson (12) on heat treated samples of powdered cobalt, and studied theoretically by A. J. C. Wilson (13). The theoretical treatment of this problem has been extended by H. Jagodzinski (14, 15, 16). Both theoretical treatments concentrate on explaining the diffuseness of  $x$ -ray reflections as a result of the probability that a stacking fault (i.e. a break in the characteristic and repeating sequence of the structure) occurs on the average at some given number of layers in the structure. The entire emphasis on these treatments has been on random stacking faults.

#### SIMULTANEOUS OCCURRENCE OF POLYTYPES AND RANDOM STACKING IN ZnS GROWN FROM VAPOR

If an ordered stacking sequence break in wurtzite generates definite polytype structures in one environment (as in the Frondel-Palache polytypes) and random stacking sequence breaks generates "one dimensional disordered" crystals (as in the Jagodzinski-Laves crystals) from another environment, then it is not surprising to discover both phenomena occurring together in crystals grown in a third environment under different conditions. We have actually encountered this condition in studies of synthetic crystals of ZnS grown from the vapor phase by F. Kremheller and D. Bracco of the Physical Chemistry Section, Physics Laboratories, Sylvania Research Center, as well as in crystals grown in vacuum by us.

H. Müller (17) has expanded the Jagodzinski treatment of relating diffuse scattering to stacking faults in crystals by introducing two constants into the  $x$ -ray intensity formula which express the probabilities that the crystal will continue to develop either a 2- or a 3-layer structure as it adds new layers during its growth. Müller's work represents an improvement over Jagodzinski in so far as a 4-layer polytype is actually used in his intensity calculations, and the intensity of its  $x$ -ray reflections are handled on the same basis as the 2- and 3-layer structures. Müller finds that it is possible to relate  $\alpha$  and  $\beta$  probability values for a few crystals such that not only calculated intensities for peak reflections agree well with experimental observations on mixed polytypes, but that the calculated intensity distribution along rows of constant  $hk$  connecting

these peaks resemble the experimentally observed ones. However, the majority of Müller's crystals, he admits, cannot be interpreted by his theoretical formula. Müller's paper contains single crystal  $x$ -ray photographs which reveal the co-existence of mixed polytypes and random disorder along  $[c]$  in ZnS. He states that he finds the Frondel and Palache 15-layer structure, which we have not found to date. We had observed the co-existence of mixed polytypes and random disorder on  $[c]$  before the appearance of Müller's paper.

#### SOME EXPERIMENTAL DATA ON VAPOR PHASE ZnS CRYSTALS

We report here the following summary of those portions of our data which contribute to a more complete understanding of the ZnS structure problem as reviewed above.

(1) *External Morphology and Growth Habit:* Many crystals tend to form interpenetrating sets of thin plates at an early state—some so oriented as to be planes of one single crystal, while others belong to different crystal individuals twinned in various ways. The subsequent growth then proceeds on, or between these initial planes to incorporate them more or less completely into a crystal mass showing many re-entrant angles and angular flutings in the zone of the hexagonal axis, and complex terraces parallel to the hexagonal basal plane. There is no suggestion of cubic symmetry or habit on any crystal so far examined regardless of internal structure shown by  $x$ -rays. The highly developed striation of faces is due to the crystal growing through stacking up thin crystal plates of hemimorphic symmetry each imperfectly registered with its neighbor. Goniometer measurements and morphology studies are naturally very difficult on such crystals. The most complex crystals were those grown in open gas stream tube furnaces in atmospheres of  $H_2S$  with hydrogen or argon from sublimed ZnS powders. The only crystals showing simple growth habit were those grown from pumped or un-pumped evacuated systems.

The morphology of our synthetic ZnS crystals will be reported in more detail when the relations between morphology and internal structure can be more fully described.

Angle tables of observed forms will be published then. In the meantime, characteristic growth habits are illustrated by the four drawings of actual crystals of Fig. 1, in which complete indices for all faces are given for the orientation of axes selected.

The position of both Miller-Bravais axes ( $a_1$  and  $a_2$ ) and gnomonic axes  $p$  and  $q$  are indicated in the top plan drawing of each crystal. The indices refer to a 2-layer hexagonal (wurtzite) cell, so oriented as to make the pyramids of  $43^\circ 21'$  and  $62^\circ 05'$  the (10.2) and (10.1) forms respec-

tively, the orientation used in Dana's (18) Seventh Edition, which fixes the common pyramid form observed on many of our crystals as (10.4).

Crystal 1A is representative of many crystals examined, in that the morphology is different for different parts of an individual crystal. The differences in external morphology can, at times, be correlated with differences in internal structure. In this example, the lower thicker portion of the crystal consists of a 3-layer structure, while the top consists of a mixture of 2-, 3-, 4- and 6-layer structures. The entire crystal is slightly under 1 mm. in length, is colorless and very transparent. Fine striations, parallel to the edges of the basal plane, encircle the entire crystal with the exception of the vertical faces of the top portion. Note that the prominent vertical forms ( $2\bar{1}.0$ ) and ( $\bar{1}2.0$ ) of the lower 3-layer structure portion are absent in the top mixed structure portion, while the prominent (10.0) and (01.0) forms of the top are absent (or nearly so) on the bottom portion. The prominent forms of the top are rotated  $30^\circ$  with respect to the prominent bottom forms. The deeply striated faces lead to complex multiple signals on the optical goniometer due to their diffraction grating behavior; so that it is frequently necessary to use narrow line signals and monochromatic light to determine the true angles on such crystals.

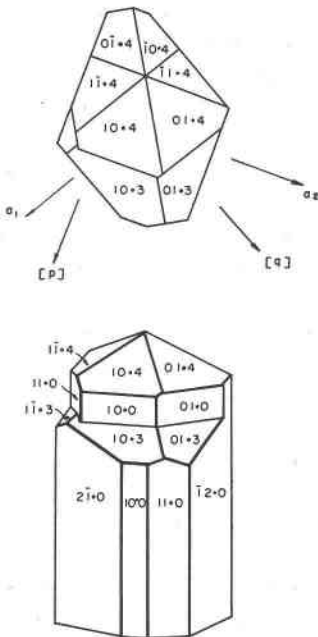
The crystal of Fig. 1B illustrates the origin of many of the typical striations present. The crystal, approximately 1 mm. high, is obviously built up of individual thin plates stacked perpendicular to  $[c]$ . Each plate, as revealed by the detail at each corner, preserving the morphology and symmetry of the whole crystal, namely, terminated on one end by pyramids of the form ( $1\bar{1}.4$ ) and on the other by ( $00.\bar{1}$ ) while joined on their basal planes. The separate faces present on the corner of the illustration continue around the entire crystal accounting for its finely striated surface which extends to all faces, including the terminal tip of the crystal. Internally the crystal is colorless and transparent. It is a further example of the terraced habit illustrated in Fig. 1A, and occurs in the same lot of material. It is composed of only 3-layer structure but there is no trace of cubic habit.

The crystal of Fig. 1C illustrates further examples of striation, not necessarily due to the same cause as in Fig. 1B, and lack of cubic growth habit in spite of 3-layer internal structure. To what extent this is due to the 3-layer structure actually being the newly discovered rhombohedral phase, has not yet been determined. In Fig. 1C, the terminal faces are not striated, and the basal plane is a good reflecting surface, but frequently not  $90^\circ$  from the vertical zone faces. Its  $\rho$  angles vary in different individuals from the same preparation from a few minutes to  $1^\circ 40'$ .

## SYNTHETIC ZnS CRYSTALS

## VAPOR PHASE GROWN

A



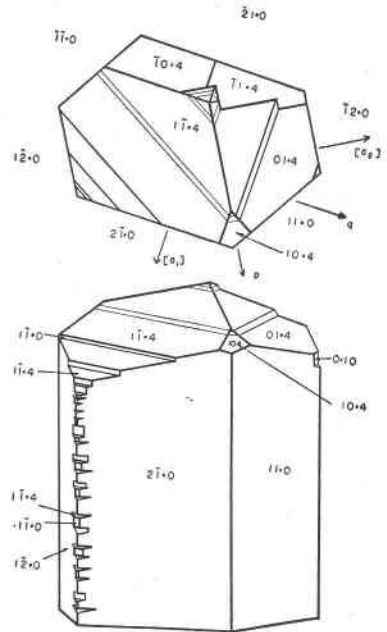
Body: 3-Layer Structure

Tip: Mixture of 2+3+4+6 Layer Structures

All Faces Striated  $\perp$  to  $[c]$ , Except Vertical Zone of Tip.

## WURTZITE INDICES

B



3-Layer Structure

Deep Striations Encircle Crystal  $\perp$  to  $[c]$ .

Composed of Many Thin Crystals and Coalesced on (001).

FIG. 1

The unique and characteristic feature of this crystal is the protruding edge which, as is evident by reference to the indexed plan drawing, is the rudiment of a (10.0) tabular habit containing the  $a_2$  and  $[c]$  axes of the crystal. The large number of faces in the  $[c]$  axis zone make these small crystals almost cylindrical in cross section and the identification of forms difficult, especially in the region of the protruding (10.0) plate. Other crystals have developed many similar protruding plates parallel to other forms, making the vertical zone of such crystals a complicated series of vertical grooves and ridges with dozens of extremely narrow faces. Obviously these fluted crystals cannot be measured accurately. Under the microscope they reveal a remarkable uniformity in the manner in which their horizontal striations cut across all the vertical surface details at

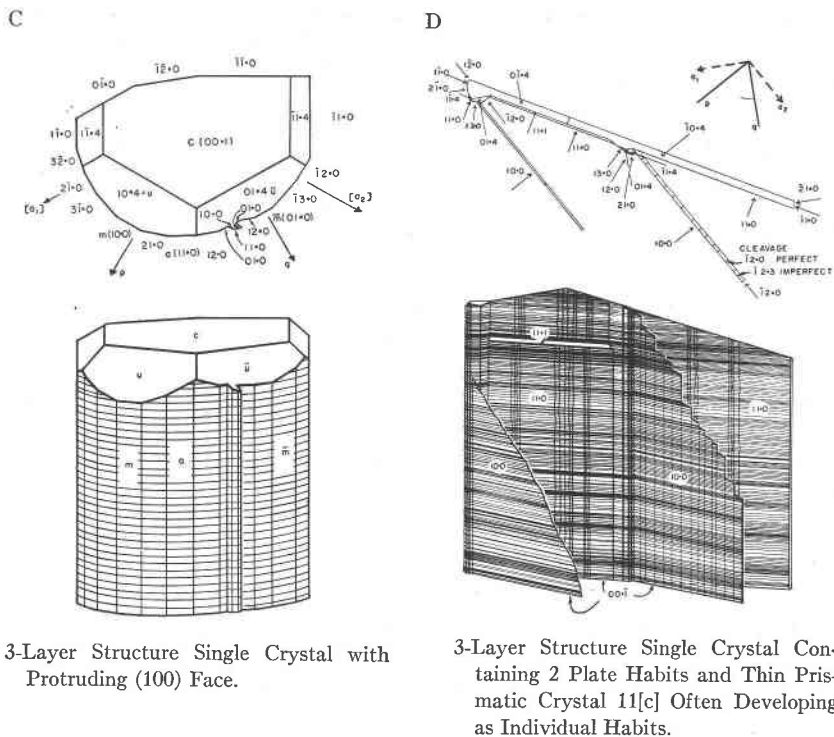


FIG. 1

the same height in the crystal, as illustrated for the single protruding (10.0) plate in Fig. 1C. The tendency to develop with only 5 of the 6 possible terminal faces of the same form is a very constant feature of this and many other lots of crystals.

The crystal of Fig. 1D also shows a pure 3-layer internal structure. Shown in comparable orientation and indexed, like the other on a  $2H$  cell, the unique feature pointed out for crystal 1C is developed to an extreme degree in 1D. The crystal has developed two tabular habits to similar extents; one parallel to (10.0), (already shown as a protruding plane in 1C) and the other parallel to (11.0). The former is approximately  $10\ \mu$  and the latter approximately  $15\ \mu$  thick. This is not a twin, as shown by  $x$ -ray measurements on each portion. The two thickened portions shown in the drawing represent regions where the material is tending to produce an independent, but slender, individual of the same habit as the crystal shown in Fig. 1C—including elongation on  $[c]$ , horizontal striations, the same terminal forms ( $u$ ), and the protruding (10.0) plate. The principal portion of the crystal (11.0) plate is terminated on top by



two ( $u$ ) faces and on the bottom by a basal plane. Although this crystal measured approximately 2 mm. in width, the thin (10.0) wing (plate  $10\ \mu$  thick) was only  $18'$  off from its theoretical angle of  $30^\circ$  from (11.0). The two (01.4) faces on the two separated thickened portions differed only by  $4'$  in measured V angle on the goniometer. The vertical ( $\bar{1}2.0$ ) cleavage is perfect, requiring only little pressure to break narrow strips from the entire length of the crystal. The imperfect cleavage indexed as ( $\bar{1}2.3$ ) is estimated from microscopic observations, as no measurements could be made on the cleavage surfaces. The wavy vertical lines indicate a local thickening of the crystal which does not progress to the point of developing definite reflecting faces. This drawing shows the single unit form (11.1) of wurtzite which was observed in a total of many hundreds of faces measured. Finally, the extreme regularity with which the horizontal striations continue at the same height of the crystal, extending to all lateral developments, is illustrated in Fig. 1D. These were observed by ordinary binocular microscopic visual observation, and on high magnification reflected light micrographs. Crystals representing each unit of this complex habit were observed in the same crystal preparation. Other equally characteristic and unique examples of morphology, growth habit, and twinning will be presented in a later paper.

(2) *X-ray Examination of Single Crystals*: A few crystals are found with a 3-layer spacing only on  $[c]$ . These were all, early in our work, listed as cubic structure, as they were by all previous workers who used powder methods. Many such 3-layer structures are undoubtedly actually rhombohedral in light of our most recent results. A few other crystals show a 2-layer spacing only on  $[c]$ , and are accordingly hexagonal. More frequently both 2- and 3-layer structures are present in varying proportions in a crystal which, microscopically, appears to be a uniform crystal entity. A striking characteristic of the crystals grown from gas-streams at atmospheric pressure by A. Kremheller of these laboratories, is that minor amounts of 4- and 6-layer structure also occur frequently in the same individuals containing 2- and 3-layered structure as their major structural component. It has already been pointed out that the top portion of the crystal illustrated in Fig. 1A has such a mixed structure. One quadrant of a single crystal rotation photograph about the  $[c]$  axis of this tip is reproduced in Fig. 2. First layer line reflections corresponding to four different structures are observed. Those from the 3-layer structure are most intense while those from the 6-layer structure are weakest. The disordered portion of the crystal accounts for the diffuse reflections appearing to join the reflections from (10 $l$ ) (01 $l$ ) and (20 $l$ ) (02 $l$ ) into an approximate continuous ring, while the (11 $l$ ) reflections are sharp in comparison and are not joined into a continuous ring of diffuse reflections.

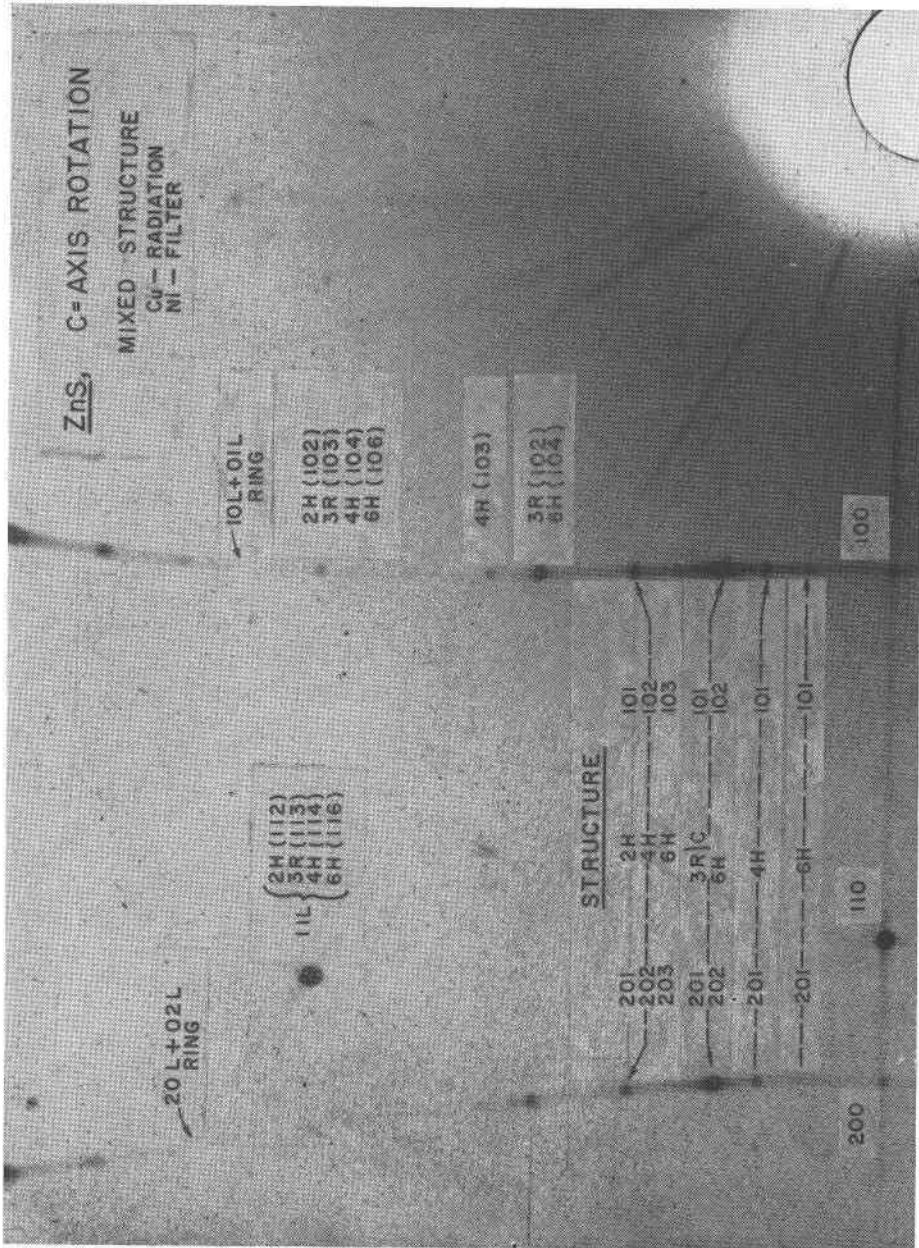


Fig. 2

The diffuse reflections thus lie in zones containing planes for which  $h+2k$  is a number not divisible by 3, while sharp reflections lie in zones where  $h+2k=n$  (3), where  $n$  is an integer or zero.

Crystals grown in evacuated systems by us have so far shown only a small amount of 6-layer structure (no 4-layer) which is distributed more randomly and in smaller parcels throughout the crystal than in case of crystals grown by Kremheller at atmospheric pressure. One small crystal (approximately  $0.01 \times 0.1$  mm.) contained nine different structures: i.e. 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 11-layered ones. The temperature of transition, and stability range of these various structures (including the cubic-hexagonal) is still being studied; as the problem is now confused by the discovery of the previously unrecognized rhombohedral intermediate phase, as well as by the unknown influence of specific impurities.

(3) *Derivation of Polytype Structures by Periodic Sequence Breaks:* Because of the large number of polytypes which have been observed in both ZnS and SiC, considerable thought has been given to the manner in which they are generated. Obviously they can form by a periodically repeated break in the basic stacking sequence, as stated above. There are two such sequences; namely, one with a periodicity of 2-layers, the other with a 3-layer periodicity on  $[c]$ . To examine the consequence of such breaks in terms of the three termed *ABC* notation is difficult. A convenient notation has been developed in a two termed *TB* notation. This *TB* notation states the orientation of the  $\text{ZnS}_4$  tetrahedra in adjacent (001) planes of all hexagonal close packed structures, and of cubic close packed structures in comparable orientation. In a 2-layer structure the tetrahedra are oriented differently in adjacent layers, which is designated as a *TB* structure. In structures containing *TBTB . . .* sequences, the tetrahedra have one face (three corners) in the (001) plane and an apex (the fourth corner) in an adjacent plane. This fourth corner belongs to a group of three corners of a tetrahedron face in the adjacent (001) plane. The tetrahedra faces are rotated  $60^\circ$  in the second plane (*T* orientation) with respect to the first plane (*B* orientation). In a 3-layer structure, the tetrahedra faces are all in the same orientation in adjacent (001) planes. The former, with a (*TB*) structure, is thus designated as possessing a *rotated sequence*; and the latter, with a (*TTT . . .* or *BBB . . .*) structure, as possessing a *parallel sequence* throughout the entire crystal in case of a pure homogeneous structure type.

We have examined the consequence of introducing breaks in each type of sequence at a progressively greater number of layers out from the initial growth layer. It is readily shown that for each type of sequence, and for each position of sequence break ( $N^*$  = number of layers from zero layer at which a break occurs), the structure will be represented by either

a hexagonal or rhombohedral lattice with a finite number of layers in its unit cell characteristic of  $N^*$ .

For example, breaking the *rotated sequence* at  $N^*=2, 4, 6, 8, \dots$  produces structures based on a hexagonal lattice with unit cells of 4-, 8-, 12-, 16-layers. Breaks at  $N^*=1, 3, 5, 7, \dots$  produce structures based on rhombohedral lattices with unit cells of 1-, 3-, 5-, 7-layers (or expressed on a hexagonal lattice with cells of 3-, 9-, 15-, 21-layers).

Corresponding breaks in the *parallel sequence* at  $N^*=1, 2, 3, 4, 5, \dots$  generates structures based on hexagonal cells, containing 2-, 4-, 6-, 8-, 10-layers.

The consequence of breaking these fundamental sequences in crystals growing in both directions along  $[c]$  have also been examined, but the results are beyond the scope of this paper. A corresponding study is underway for relating polytype structures to disorders created in a crystal already in the solid state.

We want to emphasize here our belief and preliminary observations that the value of  $N^*$  is determined primarily by the impurities in the crystal growing atmosphere. It is the first particle to attach at a growing surface which determines the structure over the entire area to which growth extends from this initial growth center, and if this particle happens to be an impurity particle, it may break an already established sequence. The kinetics of the growth process, and its relation to structure is being studied in different ZnS crystal growing atmosphere compositions.

#### CONCLUSIONS

Our studies on polytype genesis have pointed up the close relationship between random disorder and "ordered disorder" in ZnS crystals, and emphasized the need for further studies on the role of mixed polytype structures on external morphology and physical properties of zinc sulfide.

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